

DETAILED CHARACTERIZATION OF SYNTHETIC FUEL STREAMS

by

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INTRODUCTION

In depth characterization of synfuels requires the combination of several analytical tools and approaches. This requirement is due both to the complexity of the materials to be analyzed and to the information content that is desirable to obtain on semi-routine, research type samples.

Synfuels generally contain a large variety of hydrocarbons, including paraffins, cycloparaffins, aliphatic and aromatic olefins, one to eight-ring aromatics, and the corresponding aromatic furans, aromatic thiophenes, hydroxy-aromatics, dihydroxy-aromatics, aromatic pyrroles and aromatic pyridines. Minor amounts of polyfunctional components, such as thiophenofurans, hydroxy-nitrogen compounds, etc., are also present, as well as ketones, aldehydes, acids, amides, nitriles and dinitrogen compounds. Alkyl substitution of the above can range from zero to up to 50 carbon atoms. All considered, a typical synfuel sample contains as many as 1000 to 3000 carbon number homologs and many more positional isomers.

In our Laboratories, the information content required in general includes at least the identification and determination of most carbon number homologs, that is most discreet formulas, and as many individual isomers as can be separated by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS). These are numerous, in particular in the lower boiling ranges up to about C_{12} , where the number of isomers is sufficiently small to be resolved by capillary column GC.

This presentation deals with the methodology developed at our laboratories for the detailed characterization of synfuels. This methodology will be illustrated with examples taken from the detailed analysis of a standard Colorado shale oil purchased from the National Bureau of Standards (SRM 1580). Issues discussed will include separation procedures and the analysis of the separated fractions by high and low resolution mass spectrometry (HRMS and LRMS), GC/MS, nuclear magnetic resonance (NMR) and other methods.

DISCUSSION

A. Overall Procedure

The analytical scheme devised for the characterization of complex synfuels that include significant amounts of non-hydrocarbons consists essentially of a separation step followed by extensive instrumental analysis of the separated fractions. A schematic of the procedure is given in Figure 1.

The extensive separation steps used yield important information on the chemical classes of components present, enrich trace components, facilitate subsequent instrumental analyses by greatly simplifying the samples to be analyzed, and eliminate many uncertainties related to composition as the presence of a given component in one or the other fraction is a clue to its identification. For example, high resolution MS can not determine in complex mixtures whether a component whose formula contains one oxygen atom is aromatic furan or a hydroxy-aromatic; but the component can be safely assigned a furanic or a hydroxy-aromatic structure according to whether it occurs in a neutral aromatic or in an acidic fraction. The number of fractions separated depends on the amount of information desired; and varies from three (saturates, aromatics, polars) to twelve, as discussed in this presentation. Unseparated materials can also be analyzed; the loss of information content is compensated by the faster response time and lower analytical expenditure. Furthermore, composition uncertainties can be resolved reasonably well in many such cases by using assumptions based on information obtained from separated samples.

Instrumental tools used for in depth analysis of the fractions include high resolution MS, GC/MS, ^{13}C and ^1H NMR, GC distillations and elemental analyses. Data from these analyses are integrated to provide the user with a multi-faceted insight into the overall composition.

B. Separations

The separation scheme used for the NBS shale oil is shown in Figure 2. It is based largely on procedures developed at the Laramie Energy Technology Center of the Department of Energy, now Western Research Institute. Generally, the procedure yields sharp fractions, although overlaps exist, in particular between some of the aromatic and the lower polarity "polar" fractions, such as the "neutral polars". As will be shown below, most of the overlaps can be corrected by the subsequent instrumental analyses of the fractions. In fact, if, as mentioned above, separations improve the overall characterization, one can also state that the characterization steps can improve the quality of the separations by correcting for separation overlaps. Both analytical steps are necessary for in depth understanding.

Another advantage of the above separation scheme is that it isolates some components that are not generally detected by high resolution, low voltage mass spectrometry and that would be very difficult to detect by GC/MS in very complex mixtures. These are mainly the aliphatic ketones and nitriles that are found in the neutral polars, weak acids, and weak bases.

Quantitative data on the fractions separated from the NBS shale oil are given in Table I. Major components are saturates and olefins (mostly linear), strong bases, neutral polars and the 1-ring aromatics. Loss was only about 9 percent, a small amount considering that the sample contained significant concentrations of relatively low-boiling materials in the $\text{C}_8\text{-C}_{12}$ range.

The aliphatic fraction was separated further into saturates and olefins. Although the purity of the fractions was high, recovery was low. For this reason, quantitative data were obtained on total aliphatics.

C. Instrumental Analysis

The aliphatic fractions were analyzed by low resolution, high voltage MS, GC/MS, ^1H and ^{13}C NMR. All other fractions were analyzed by the same methods, except that the MS analyses were obtained in the much more powerful high resolution, low voltage mode, rather than under low resolution, high voltage conditions.

The type of information available from the above methods is summarized.

Low Resolution, High Voltage MS: Concentration of saturate and aromatic compound types (homologous series). In the present work, the approach was used only on the aliphatic fraction. A major disadvantage is the impossibility of distinguishing cycloparaffins from olefins, dicycloparaffins from cyclic olefins or diolefins, etc., due to the fact that they have the same general formulas.

High Resolution, Low Voltage MS: Concentration of aromatic and polar aromatic carbon number homologs. The method can determine several thousand components per sample, including hydrocarbons and heterocompounds and yields both very detailed and summarized data. Its main disadvantage is that it cannot be applied to aliphatic components.

GC/MS: Identifications and semi-quantitative analysis of individual components -- usually several isomers for each carbon number homolog. Applicable to both aromatic and aliphatic components, but limited by the resolution of the GC and the MS, boiling point and the unavailability of reference spectra for many of the components found in shale oils.

^{13}C and ^1H NMR: Overall saturate, olefinic or aromatic character; semi-quantitative insight into average structural features.

D. Typical Results

The major compound types determined in the various fractions are listed in Table II. The wide variety is an indication of the complexity of the shale oil studied. Most of the hydrocarbons, furans, thiophenes, hydroxy-aromatics and aromatic nitrogen types were detected both by high resolution MS and GC/MS. Some of the more condensed materials were determined only by high resolution MS; conversely aliphatic polar types such as ketones and nitriles were seen only by the GC/MS as these materials generally do not give significant molecular ions at low voltages.

A summary of the high resolution MS analyses of the fractions is given in Tables III-V. Most of the data is self-explanatory; several comments are, however, in order.

- Overall condensation is low; most of the components are either linear, or contain one or two aromatic or polar aromatic rings.
- Separation is rather sharp in most of the fractions; including the aromatic sub-fractions. Aromatic overlaps found mainly in the "less polar" polar fractions, such as the weak bases and the neutral polars, and these aromatics are the most condensed types, that indeed possess

some polar (basic) character. As most of the aliphatic polars not seen by high resolution MS are concentrated in these same fractions, they are probably more enriched in polar components than indicated by the high resolution MS data.

- Asphaltenes contain a very large amount of non-volatile components. We are now developing quantitative methods for determining at least the molecular weight distribution of this type of materials in the 500-3000+ molecular weight range using field desorption mass spectrometry.

Selected NMR parameters of the fractions are shown in Table VI. Aromatic character increases, as expected, with nominal condensation, in good agreement with the MS data. Fractions that contain aliphatic polars, such as the neutral polars and the bases have lower aromaticity, as expected. In general, the NMR analyses confirm the efficiency of the separations. The consistency of the NMR characterization is evident from the very good agreement between the experimental data obtained on the total sample before the separation and the composite values calculated from the eleven fractions analyzed separately (Table VII).

The GC/MS procedure is illustrated by partial chromatograms of the aliphatic (saturates plus olefins) and the neutral polar fraction that contains nitriles and ketones (Figures 3, 4). The composition pattern shown repeats itself in the higher carbon number range, up to about C₂₅-C₃₀.

The ideal analytical approach in this type of effort is the integration of all the analytical data. This is implicit in the data reported in the previous sections. A more explicit procedure is to identify as many individual isomers of a given carbon number homolog, say C₁₀ benzenes or C₇ pyridines, as possible by GC/MS and then to normalize this data to the total concentration of the homolog as determined by high resolution MS, using these powerful techniques in a complementary way. The validity of the approach is confirmed by the data in Table VIII that shows good agreement between quantitative HRMS data on the total carbon number homologs and the sums of the corresponding isomers as determined by GC/MS. One can thus assume that if the high resolution MS data on a given carbon number homolog show much higher values than the corresponding sums of the isomers found by GC/MS, the deviation is due to isomers not detected by GC/MS.

CONCLUSION

The data reported in this work show that very complex mixtures, such as synfuels, can be characterized accurately and in great detail by a combination of analytical techniques. This multitechnique approach is essential for any in depth understanding of the composition of these materials. Much more work is needed to corroborate and to extend the information gathered in this work but we believe we have the means to do so.

Table I

NBS SRM 1580 SHALE OIL PREP LC DATA

<u>Fraction</u>	<u>Weight Percent</u>
Asphaltenes	1.60%
Weak Acids	5.00%
Strong Acids	0.15%
Weak Bases	1.84%
Strong Bases	15.43%
Saturates + Nonaromatic Olefins	34.05%
1-Ring Aromatics	8.10%
1-2 Ring Aromatics	5.05%
2-3 Ring Aromatics	1.84%
3+ Ring Aromatics	0.89%
Neutral Polars	16.46%
Hold-Up & Losses	<u>9.28%</u>
Total	100.00%

Table II

MAJOR COMPOUND TYPES IN NBS SHALE OILS FRACTIONS

- | | |
|---|---|
| <p>1. <u>Saturate Fraction</u>
 n-Paraffins
 Isoprenoid Paraffins
 Cycloparaffins</p> | <p>7. <u>Neutral Polar Fraction</u>
 Linear Cyclic Ketones
 Aliphatic & Nitriles
 Benzonitriles/Indoles</p> |
| <p>2. <u>Olefin Fraction</u>
 Alpha Olefins
 Internal Olefins</p> | <p>8. <u>Weak Acid Fraction</u>
 Phenols
 Carbazoles
 Pyrroles
 Aliphatic Nitriles</p> |
| <p>3. <u>"1-Ring Aromatic" Fraction</u>
 Benzenes
 Styrenes
 Indans/Tetralins
 Thiophenes</p> | <p>9. <u>Strong Acid Fraction</u>
 Phenols
 Hydroxy-Indans/Tetralins
 Carbazoles</p> |
| <p>4. <u>"2-Ring Aromatic" Fraction</u>
 Indans, Tetralins
 Indenes
 Naphthalenes
 Biphenyls
 Acenaphthenes
 Benzothiophenes
 Benzofurans</p> | <p>10. <u>Weak Base Fraction</u>
 Nitriles
 2-Ketones
 Acetophenones</p> |
| <p>5. <u>"3-Ring Aromatic" Fraction</u>
 Naphthalenes
 Biphenyls
 Fluorenes
 Phenanthrenes
 Pyrenes</p> | <p>11. <u>Strong Base Fraction</u>
 Pyridines
 Quinolines
 Tetrahydroquinolines
 Tetrahydrocarbazoles</p> |
| <p>6. <u>"3+Ring Aromatic" Fraction</u>
 Phenanthrenes
 Chrysenes
 Benzoanthracenes</p> | <p>12. <u>Asphaltenes</u>
 Non-Volatiles
 1-3 Ring Nitrogen Compounds</p> |

Table III

SUMMARY COMPOSITION OF NEUTRAL FRACTIONS AS DETERMINED BY
HIGH AND LOW RESOLUTION MS

<u>Component Type</u>	<u>Weight Percent</u>				
	<u>Aliphatics</u>	<u>Aromatics</u>			
		<u>1 Ring</u>	<u>2 Ring</u>	<u>3 Ring</u>	<u>4 Ring</u>
Aliphatics	95.6	0.0	0.0	0.0	0.0
Aromatic Hydrocarbons	4.4	82.2	87.0	83.6	78.7
1 Ring	4.4	73.1	16.8	1.4	3.1
2 Ring	0.0	9.2	62.3	29.1	12.1
3 Ring	0.0	0.0	6.9	42.9	38.0
4 Ring	0.0	0.0	0.9	9.6	24.9
5+Ring	0.0	0.0	0.1	0.6	0.6
Aromatic Thiophenes	0.0	17.5	7.4	7.1	8.8
1 Ring	0.0	15.5	0.2	1.4	2.9
2 Ring	0.0	2.0	6.3	5.6	2.9
3+Ring	0.0	0.0	0.9	0.1	3.0
Aromatic Furans	0.0	0.3	4.0	5.7	3.1
1 Ring	0.0	0.3	2.3	1.0	0.0
2 Ring	0.0	0.0	1.6	3.4	0.5
3 Ring	0.0	0.0	0.1	0.7	1.1
4+Ring	0.0	0.0	0.0	0.6	1.5
Aromatic Difurans	0.0	0.0	0.0	0.3	1.5
Nitrogen Cpds.	0.0	0.0	1.6	3.3	6.3
Residue	0.0	0.0	0.0	0.0	1.6

Table IV

SUMMARY COMPOSITION OF POLAR FRACTIONS AS DETERMINED BY HIGH RESOLUTION MS

Component Type	Weight Percent					Asphaltenes
	Neutral Polars	Weak Acids	Strong Acids	Weak Bases	Strong Bases	
Mono-Oxygen Cpds. (mostly hydroxy- aromatics)	<u>11.9</u>	<u>15.2</u>	<u>43.4</u>	<u>4.1</u>	<u>0.2</u>	<u>1.7</u>
1 Ring	9.2	11.7	35.6	2.8	0.1	0.7
2 Ring	1.4	2.1	6.4	1.1	0.1	0.8
3 Ring	0.8	0.6	1.3	0.2	0.0	0.2
4+Ring	0.5	0.8	0.1	0.0	0.0	traces
Di-Oxygen Cpds. (mostly dihydroxy- aromatics)	<u>0.0</u>	<u>2.5</u>	<u>6.0</u>	<u>0.0</u>	<u>0.0</u>	<u>0.6</u>
1 Ring	0.0	1.7	4.5	0.0	0.0	0.5
2+Ring	0.0	0.8	1.5	0.0	0.0	0.1
Nitrogen Cpds.	<u>57.1</u>	<u>54.0</u>	<u>8.5</u>	<u>63.1</u>	<u>88.0</u>	<u>10.5</u>
1 Ring	<u>2.2</u>	<u>5.2</u>	<u>0.3</u>	<u>4.3</u>	<u>45.3</u>	<u>1.9</u>
2 Ring	37.4	25.0	3.0	30.5	25.6	5.0
3 Ring	15.5	18.2	4.6	22.6	13.5	3.0
4+Ring	2.0	5.6	0.6	5.7	3.6	0.6
Nitrogen-Oxygen Cpds.	<u>0.7</u>	<u>3.5</u>	<u>10.4</u>	<u>4.9</u>	<u>0.4</u>	<u>1.4</u>
1 Ring	<u>0.1</u>	<u>1.4</u>	<u>6.9</u>	<u>1.0</u>	<u>0.1</u>	<u>0.4</u>
2 Ring	0.3	1.4	2.9	2.3	0.1	0.8
3+Ring	0.3	0.7	0.6	1.6	0.2	0.2
Misc. N. Compounds	<u>0.4</u>	<u>3.0</u>	<u>1.2</u>	<u>0.0</u>	<u>2.0</u>	<u>1.0</u>
Aromatic Hydrocarbons	<u>22.0</u>	<u>2.1</u>	<u>0.5</u>	<u>7.0</u>	<u>1.9</u>	<u>0.3</u>
1-3 Ring	<u>6.5</u>	<u>2.1</u>	<u>0.4</u>	<u>1.9</u>	<u>1.7</u>	<u>0.2</u>
4-6 Ring	15.5	0.5	0.1	5.1	0.2	0.1
Thiophenes	<u>0.3</u>	<u>0.3</u>	<u>0.2</u>	<u>0.2</u>	<u>0.0</u>	<u>Traces</u>
Furans	<u>0.0</u>	<u>0.0</u>	<u>0.0</u>	<u>0.0</u>	<u>0.0</u>	<u>0.0</u>
Residue	<u>7.6</u>	<u>19.4</u>	<u>29.8</u>	<u>20.6</u>	<u>7.5</u>	<u>84.5</u>

Table V

SUMMARY COMPOSITION OF SHALE OIL AS CALCULATED FROM ANALYSES OF FRACTIONS

<u>Component</u>	<u>Wt. Pct.</u>	<u>Component</u>	<u>Wt. Pct.</u>
<u>Aliphatics</u>	<u>32.53</u>	<u>Polar Aromatics</u>	<u>31.49</u>
<u>Neutral Aromatics</u>	<u>21.43</u>	<u>Mono-Oxygen Cpds.</u>	<u>3.04</u>
<u>Hydrocarbons</u>	<u>18.98</u>	1 Ring	2.35
1 Ring	8.86	2 Ring	0.41
2 Ring	4.94	3 Ring	0.17
3 Ring	2.01	4+Ring	0.11
4 Ring	2.76	<u>Di-Oxygen Cpds.</u>	<u>0.16</u>
5+Ring	0.41	1 Ring	0.11
<u>Thiophenes</u>	<u>2.07</u>	2 Ring	0.04
1 Ring	1.33	3+Ring	0.01
2 Ring	0.63	<u>Nitrogen Cpds.</u>	<u>27.23</u>
3 Ring	0.10	1 Ring	7.74
4+Ring	0.01	2 Ring	12.08
<u>Furans</u>	<u>0.36</u>	3 Ring	6.12
1 Ring	0.16	4+Ring	1.29
2 Ring	0.14	<u>Nitrogen-Oxygen Cpds.</u>	<u>0.51</u>
3 Ring	0.02	1 Ring	0.14
4+Ring	0.04	2 Ring	0.21
<u>Difurans</u>	<u>0.02</u>	3+Ring	0.15
		<u>Misc./Nitrogen Cpds.</u>	<u>0.55</u>
		<u>Residue</u>	<u>5.27</u>
		<u>Separation Loss</u>	<u>9.28</u>

Table VI
SELECTED NMR DATA ON FRACTIONS

<u>Carbon Type</u>	<u>Mole Percent</u>							
	<u>Aliphatics</u>	<u>Aromatics</u>			<u>Neutral Polars</u>	<u>Acids</u>	<u>Bases</u>	<u>Asphaltenes</u>
		<u>1 Ring</u>	<u>2 Ring</u>	<u>3 Ring</u>				
Aromatics	0.0	33.5	54.2	54.3	33.0	55.1	40.4	66.3
Olefinic	2.3	1.4	0.0	0.0	0.0	0.0	0.0	0.0
Aliphatic	97.6	65.2	45.8	45.7	67.0	44.9	59.6	33.7

Table VII
COMPARISON OF NMR DATA ON FRACTIONS AND TOTAL SAMPLE

<u>Carbon Type</u>	<u>Mole Percent</u>	
	<u>Composite Calculated from Fractions</u>	<u>Experimental Value Found for Total Sample</u>
Aromatic	25.8	27.2
Olefinic	1.0	1.6
Aliphatic	73.2	71.2

Table VIII

COMPARISON OF HIGH RESOLUTION MS (HRMS) AND GC/MS DATA
ON SELECTED COMPONENTS IN VARIOUS FRACTIONS

<u>Components</u>	<u>Concentration</u>		<u>No. of Components</u>
	<u>HRMS</u>	<u>GC/MS</u>	
<u>Alkylbenzenes, wt. pct.</u>			
C ₈	0.48	0.25	4
C ₉	1.27	1.42	8
C ₁₀	6.06	6.61	17
C ₁₁	7.02	6.34	19
C ₁₂	2.90	2.53	26
<u>Phenols, ppm</u>			
C ₆	4.3	8.0	1
C ₇	28.4	26.0	3
C ₈	16.9	17.8	6
<u>Pyridines, wt. pct.</u>			
C ₅	0.10	0.19	1
C ₆	1.02	1.11	3
C ₇	0.69	0.60	9
C ₈	0.19	0.10	4

FIGURE 1
OVERALL ANALYTICAL APPROACH

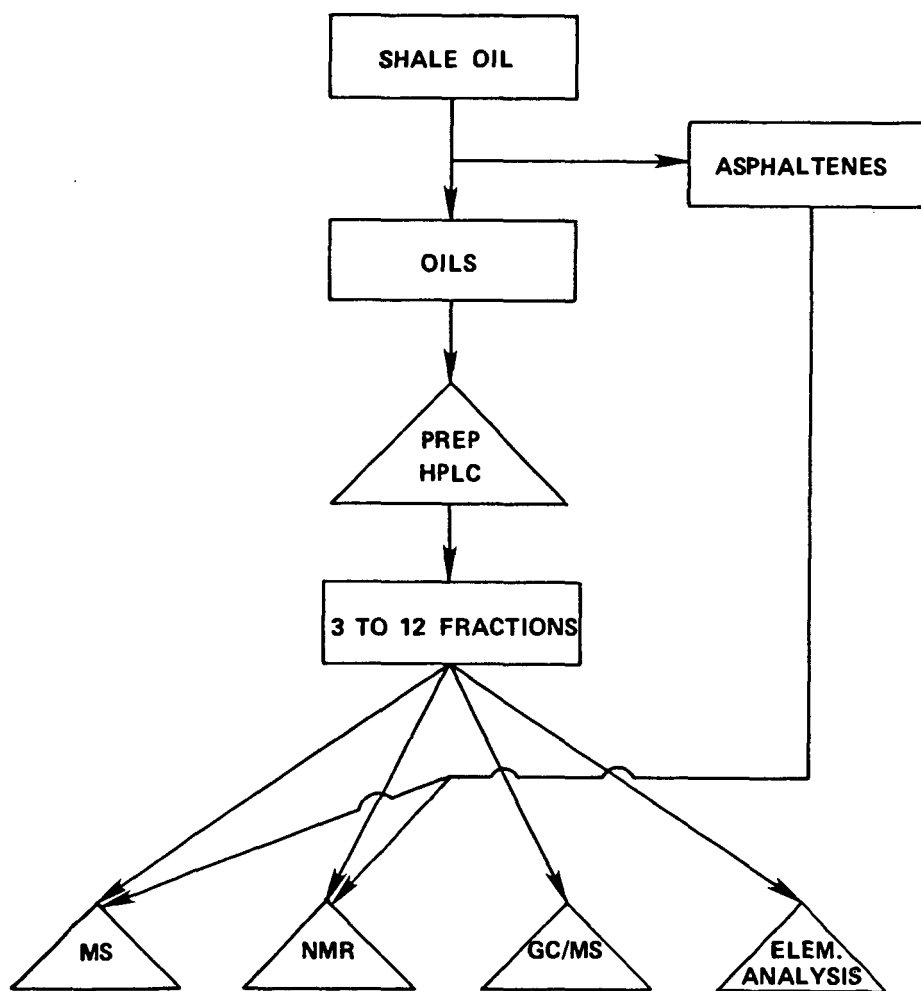
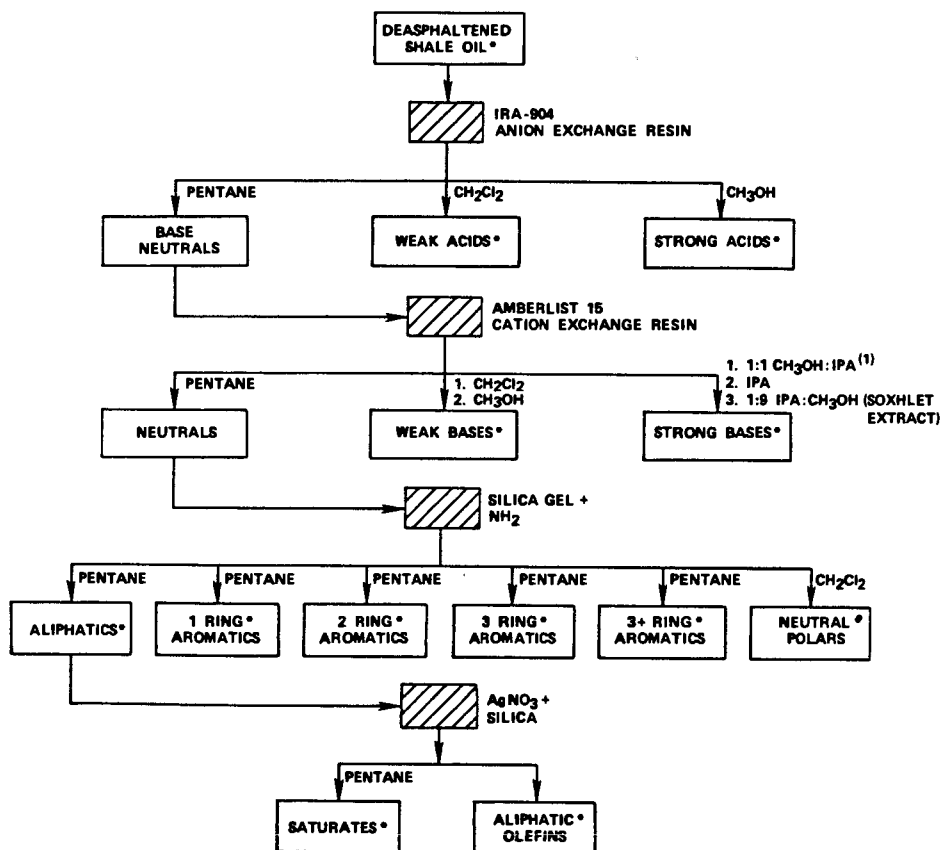


FIGURE 2
DETAILED SEPARATION SCHEME



* FRACTIONS SUBMITTED TO INSTRUMENTAL ANALYSES (MS, GC/MS, NMR, ETC.)

(1) ISOPROPYL-AMINE

FIGURE 3

PARTIAL GC/MS CHROMATOGRAM OF MBS SHALE OIL
SATURATES & OLEFINS

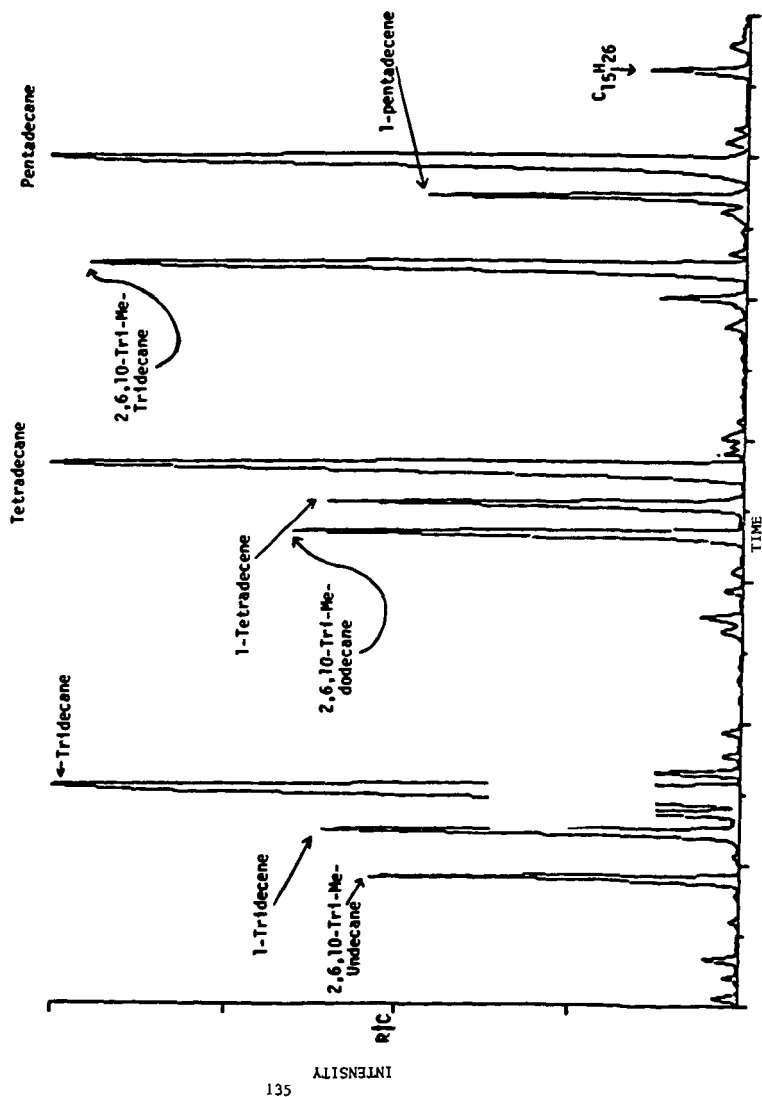


FIGURE 4

PARTIAL GC/MS CHROMATOGRAM OF MBS SHALE OIL
NEUTRAL POLARS

